

PATENT SPECIFICATION

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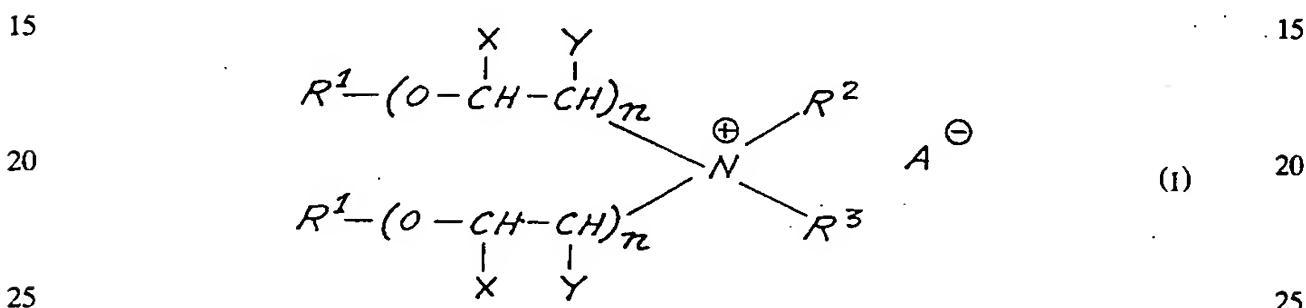
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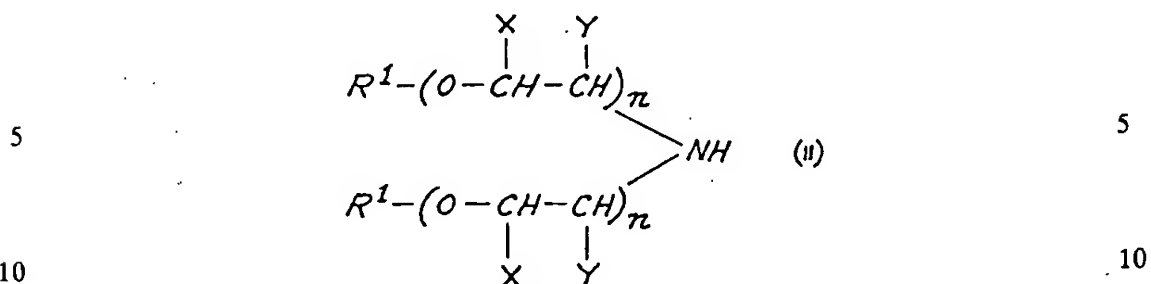
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(54) QUATERNARY AMMONIUM COMPOUNDS. PROCESS FOR THEIR PREPARATION AND COMPOSITIONS CONTAINING THEM

- 5 (71) We, HOECHST AKTIENGESellschaft, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: 5
 10 This invention relates to quaternary ammonium compounds, to a process for preparing them and to hair care and fabric softening compositions containing them.
 The present invention provides quaternary ammonium compounds of the general formula



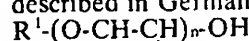
- in which each R¹ is an alkyl or alkenyl group having from 8 to 30 carbon atoms, preferably from 14 to 24 carbon atoms, a cyclohexyl group or an aryl group which may be substituted by one or more alkyl groups, each X and Y is a hydrogen atom or a methyl group with the proviso that X and Y cannot both be methyl groups in the same alkyleneoxy group, each n is an integer from 1 to 20, preferably from 1 to 5, each of R² and R³ is a benzyl group or an alkyl group having from 1 to 4 carbon atoms, preferably a methyl group, and A[⊖] is a methylsulfate, ethylsulfate, methylphosphate, bromide or, preferably, chloride ion. 30
 These compounds are prepared in accordance with the present invention by quaternization of one mole of secondary ether amine of the general formula 35



with one mole each of compounds of the formulae R^2A and R^3A , such as alkyl chloride or bromide, alkyl sulfate or benzyl chloride, in the presence of an alkali metal base.

The reaction is preferably carried out at an elevated temperature of from 30 to 160°C in a solvent, for example water, an alcohol, for example, ethanol or isopropanol, an aromatic hydrocarbon, such as toluene or xylene, or in a polar aprotic solvent, for example, dimethylformamide, and in the presence of an alkali metal base, such as sodium hydroxide, sodium carbonate or sodium bicarbonate; however, the reaction may be carried out at room temperature or without a solvent. In order to obtain uncoloured products, it is advantageous to carry out the reaction in the presence of an inert gas, for example, nitrogen.

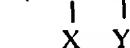
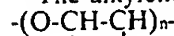
The secondary ether amines of the formula (II) can be obtained according to the process described in German Offenlegungsschrift 2555895 by reacting alkoxylates of the formula



in which R^1 , X, Y and n have the meanings given above, in the liquid phase with ammonia and hydrogen in the presence of a hydrogenation-dehydrogenation catalyst, especially a nickel or cobalt catalyst, at a gas rate of at least 10 l/kg of oxalkylate/h at a temperature of from 150 to 250°C and under a pressure of from 0.5 to 1.5 atmospheres gauge, and by eliminating the water of the reaction with the gas stream.

When R^1 is an alkyl or alkenyl group, the saturated and unsaturated alcohols upon which the alkoxy and alkenyloxy derivatives of the formula III are based and which form the group R^1 in the compounds of the formula I, may contain a primary, secondary or tertiary alcohol group. The alkyl or alkenyl group may be straight-chained or branched and is derived from a corresponding alcohol, for example, octyl alcohol, isononyl alcohol, lauryl alcohol, isotridecyl alcohol, isotridecyl alcohol, oleyl alcohol and stearyl alcohol. There may also be used mixtures of any two or more such alcohols, especially those which are formed by hydrogenation of natural fatty acids and/or their esters, for example, tallow fat alcohols, palm oil alcohols and coconut oil alcohols. Other alcohols from which the group R^1 may be derived are those which are obtained in industrial processes, for example, according to the Ziegler process (ethylene synthesis) which yields saturated primary alcohols having a straight carbon chain of up to 24 carbon atoms, and according to the various oxo processes which produce more or less branched alcohols. In addition, the group R^1 may be derived from aromatic hydroxy compounds, such as phenol, naphthols, 2,4,6-tri-tertiary butyl-phenol, 4-i-nonylphenol, 4-i-octylphenol, 4-i-propylphenol, cresol, xyleneol and 4-i-dodecylphenol, or from cyclohexanol.

The alkyleneoxy group



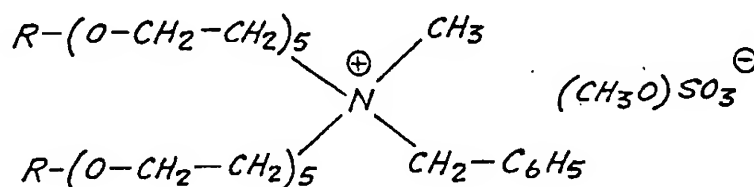
is preferably derived from ethylene or propylene oxide and is introduced by reaction of the above alcohols and aromatic hydroxy compounds with ethylene- and/or propylene oxide. In this process there may also be used mixtures of ethylene oxide and propylene oxide, or the reaction may be effected first with ethylene oxide and then with propylene oxide.

The quaternary ammonium compounds of the present invention exhibit interesting surface-active properties which makes them suitable especially as components of hair care compositions. They are miscible with water and/or ethyl alcohol in all ratios. Those compounds having a higher degree of ethoxylation (about 10 to 20 units of ethylene oxide) yield clear solutions, whereas the compounds having a lower ethoxy content (up to 8 units of ethylene oxide) are easily dispersible to give turbid solutions. However, they are equally suitable as hair care compositions in either case.

Thus, liquid or pasty hair care compositions (so-called clear-rinse and cream-rinse compositions) with a good storage stability may be prepared simply by mixing the compounds with water. Any undesired excess of quaternary ether amine can be removed from the hair without

EXAMPLE 2:

200 Parts of a secondary etheramine of a molecular weight of 854, which is obtained by the aminolysis of a coconut oil alcohol reacted with 5 moles of ethylene oxide, 250 parts of dimethylformamide, 80 parts of sodium bicarbonate and 33.2 parts of benzylchloride are stirred in a reaction flask provided with stirrer and dropping funnel for 24 hours at 80° C. After filtration and elimination of the dimethylformamide by distillation, an amine is obtained which is less than 1 % secondary and more than 99 % tertiary. The reaction of this product with 32 parts of dimethylsulfate at 60° C and while stirring for 2 hours yields a readily water-soluble quaternary ammonium compound in a yield of 99 %, whose basic-nitrogen content is 0 % and which corresponds to the following formula:



R = coco-alkyl

The basic-nitrogen content of the starting compound was 1.64 %; in the final product it is 0 %. This final value was also found in all following Examples.

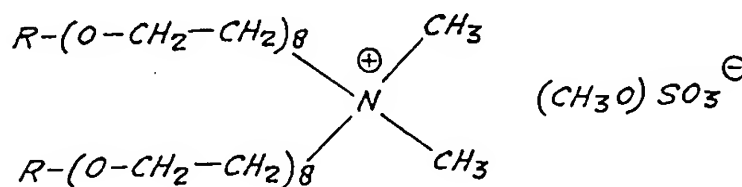
EXAMPLE 3:

400 Parts of a secondary etheramine, molecular weight 787, which is obtained by the aminolysis of a straight-chain C₂₀ 22-alcohol oxethylated with 2 moles of alkylene oxide, are heated with 30.3 parts of sodium hydroxide and 40 parts of water in a laboratory autoclave having a capacity of 2 liters at a temperature in the range of from 70 to 80° C. during which methyl chloride is forced into the autoclave up to a pressure of 5 kp/cm². When no more methyl chloride is absorbed by the reaction mixture, the autoclave is opened and the product is poured off. The degree of quaternization is 93 %, and 1 % of the product is free amine, and 6 % are ammonium hydrochloride. The product can be emulsified in water; its 1 % aqueous solution shows a pH value of from 4 to 5.

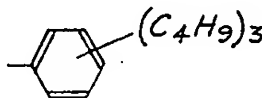
The basic-nitrogen content of the starting compound is 1.78 %.

EXAMPLE 4:

100 Parts of a secondary etheramine, molecular weight 1209, which is obtained by the aminolysis of a tributylphenol oxethylated with 8 moles of ethylene oxide, are quaternized in 100 parts of toluene, while adding 40 parts of sodium carbonate, and two 11.4 part portions of dimethylsulfate, in accordance with the procedure described in Example 1. The quaternary ammonium salt of the formula



R = tributylphenyl



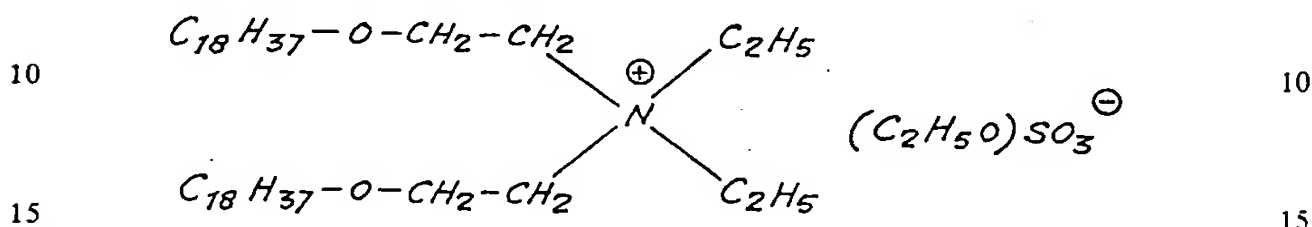
is obtained in a yield of 98 %; the basic-nitrogen content of the starting compound is 1.16 %.

EXAMPLE 5:

100 Parts of a secondary etheramine, molecular weight 952, which is obtained by the aminolysis of a straight-chain C₂₀ 22 alcohol reacted with 1 mole each of ethylene oxide and propylene oxide, are quaternized in 100 parts of toluene, while adding 40 parts of sodium carbonate, and two 14.5 part portions of dimethylsulfate in accordance with the procedure described in Example 1.

The basic-nitrogen content of the starting compound is 1.47 %.

100 Parts of a secondary etheramine, molecular weight 615, which is obtained by the aminolysis of a stearyl alcohol reacted with 1 mol of ethylene oxide, are quaternized in 100 parts of toluene, while adding 40 parts of sodium carbonate, and two 27.5 part portions of diethyl sulfate, in accordance with the procedure described in Example 1. A product which contains no basic nitrogen and which corresponds to the formula



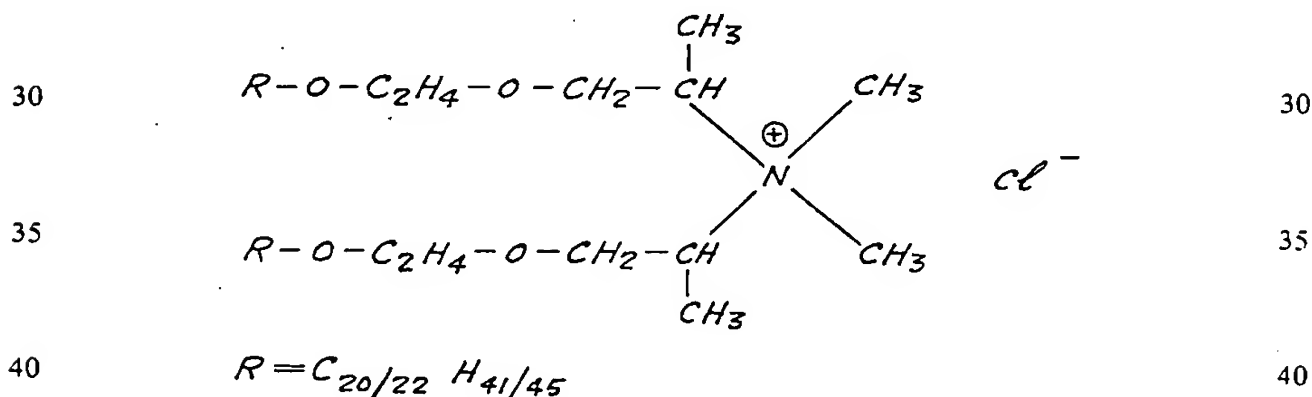
is obtained in a yield of 98 %.

The basic-nitrogen content of the starting compound is 2.27 %.

EXAMPLE 7:

200 Parts of a secondary etheramine, molecular weight 952, which is obtained by the aminolysis of a straight-chain C_{20} alcohol reacted with 1 mole each of ethylene oxide and propylene oxide, are quaternized, in the manner described in Example 3; using 8.4 parts of sodium hydroxide and 16.8 parts of water, with methyl chloride.

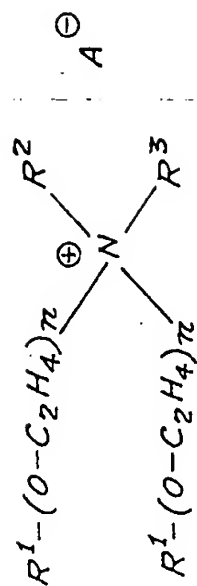
A product of the formula



is obtained in a yield of 99 %. The degree of quaternization is 92 %.

The basic-nitrogen content of the starting compound is 1.47 %.

In a manner analogous to that described in Examples 1 to 7, there are also prepared the novel quaternary ammonium compounds specified in the following Table.



content of ni-
trogen showing
an alkaline
reaction in
the starting
compound

R ¹	n	R ²	R ³	A [⊖]	content of ni- trogen showing an alkaline reaction in the starting compound
(C ₁ H ₅) ₃ -C ₆ H ₅	2	CH ₃	CH ₃	(CH ₃ O)SO ₃	1.79
"	4	CH ₃	CH ₃	"	1.54
"	8	CH ₃	CH ₃	"	1.16
"	5	CH ₃	CH ₃	"	1.64
n-C ₉ H ₁₉ -C ₆ H ₅	10	CH ₃	CH ₃	"	0.97
cyclohexyl	6	C ₂ H ₅	CH ₃	(C ₂ H ₅ O)SO ₃	1.72
C _{8/10} (43 % of C ₈ ; 55 % of C ₁₀)	2	CH ₃	C ₂ H ₅	(CH ₃ O)SO ₃	2.84
"	10	CH ₃	CH ₃	"	1.17
"	3	CH ₃	CH ₃	Cl	2.17
C ₁₂₋₁₄ (54 % of C ₁₂ ; 44 % of C ₁₄)	3	CH ₃	CH ₃	Cl	2.15
C _{12/14} (33 % of C ₁₂ ; 64 % of C ₁₄)	3	CH ₃	CH ₃	(CH ₃ O)SO ₃	2.13
isotridecyl	6	CH ₃	CH ₃	"	1.53
"	10	CH ₃	CH ₃	"	1.09
coconut oil alkyl	2	CH ₃	CH ₃	Cl	2.38
"	10	CH ₃	CH ₃	"	0.99
"	20	CH ₃	CH ₃	"	0.67
tallow fat alkyl	5	CH ₃	CH ₃	"	2.25
"	8	CH ₃	CH ₃	"	1.22
"	15	CH ₃	CH ₃	"	0.70
oleyl	2	CH ₃	CH ₃	"	2.01
"	8	CH ₃	CH ₃	"	1.12
"	10	CH ₃	CH ₃	"	0.97
"	12	CH ₃	CH ₃	Cl	0.85
"	15	CH ₃	CH ₃	Cl	0.66

The basic-nitrogen content of the final product was 0 % in all cases, so that a complete quaternization had been reached.

The following Table compares the foaming properties, measured according to the method of DIN 53 902, of the known compounds cetyltrimethyl ammonium chloride, cetyltrimethyl ammonium bromide and stearyl-pentaoxyethyl ammonium chloride with that of a quaternary etheramine compound according to the present invention, measured at 20 ° C after 25 strokes in a water of a hardness of 20° dH (German hardness) and a concentration of the active ingredient of 0.1 %.

5	Cetyltrimethyl ammonium chloride, $C_{16}H_{33}N(CH_3)_3Cl$: 740 cm ³	
10	cetyltrimethyl ammonium bromide, $C_{16}H_{33}N(CH_3)_3Br$:	10
	stearyl-pentaoxyethyl ammonium chloride $C_{18}H_{37}(OCH_2CH_2)_5NH_3Cl$: 490 cm ³	
	quaternary etheramine compound of the constitution:	
	di)decaoxyethylol- dimethyl ammonium chloride,	
	$[C_{18}H_{35}(OCH_2CH_2)_{10}]_2N(CH_3)_2Cl$: 40 cm ³	

The following Application Examples illustrate various methods of using the quaternary etheramines for the preparation of cationic hair care compositions.

The quantitative data and the percentages in the following Examples are by weight.

EXAMPLE 8:

Clear, hair-rinsing composition of low viscosity:

20	1 % of di(pentadecaoxyethylol-yl)-dimethyl ammonium chloride	20
	add 100 % of water	

EXAMPLE 9:

Clear, liquid, hair-rinsing composition of high viscosity:

25	1.5 % of di(decaoxyethylol-yl)-dimethyl ammonium chloride	
	1.0 % of hydroxyethyl cellulose	25
	0.3 % of perfume oil	
	ad 100 % of water	

EXAMPLE 10:

Liquid, hair-setting lotion:

30	3.5 % of vinylpyrrolidone-vinylacetate copolymer in the ratio of 60:40	30
	0.2 % of di-isopropyl adipate	
	0.3 % of perfume oil	
45	% of isopropyl alcohol	
	0.2 % of di(pentadecaoxyethylol-yl)-dimethyl-ammonium-methyl-sulfate	
35	ad 100 % of water	35

EXAMPLE 11:

Hair lotion:

	0.2 % of di(dodecaoxyethylol-yl)-dimethyl-ammonium-methyl -sulfate	
30	% of ethyl alcohol	
40	0.4 % of di-isopropyl adipate	40
	0.2 % of perfume oil	
	ad 100 % of water	

EXAMPLE 12:

Shampoo:

45	1.4 % of di(decaoxyethylol-yl)-dimethyl-ammonium -ethyl-sulfate	45
15	% of lauryldiglycol-ethersulfate-sodium salt	
	3 % of coconut oil acid-diethanolamide	
	0.3 % of perfume oil	
	1.2 % of sodium chloride	
50	0.1 % of formalin	50
	ad 100 % of water	

EXAMPLE 13:

Hair-rinsing composition in emulsion form:

55	2 % of di(pentadecaoxyethylstearyl) -dimethyl-ammonium-methyl -sulfate	
	3 % of stearyl alcohol + 10 moles of ethylene oxide	55
	2 % of triethylene-glycol-distearate	
	3 % of cetyl alcohol	
	0.1 % of perfume oil	
	ad 100 % of water	

EXAMPLE 14:

Hair-rinsing composition in cream form:

0.5 % of distearyl-dimethyl-ammonium chloride

1 % of di(dodecaoxyethyloleyl)-dimethyl-ammonium chloride

5 3 % of cetyl/stearyl alcohol + 9 moles of ethylene oxide 5

4 % of cetyl alcohol

0.2 % of perfume oil

ad 100 % of water

EXAMPLE 15:

10 Hairdressing cream: 10

0.2 % of di(decaoxyethyloleyl)-dimethyl -ammonium chloride

5 % of diglycerol sesquioleate

15 % of paraffin wax

1 % of silicone oil

15 15 % of Vaseline (registered Trade Mark) 15

2 % of paraffin oil

0.1 % of perfume oil

ad 100 % of water

EXAMPLE 16:

20 Hair spray: 20

1.5 % of polyvinylpyrrolidone/vinylacetate copolymer, ratio of 70:30

0.1 % of perfume oil

0.1 % of silicone oil

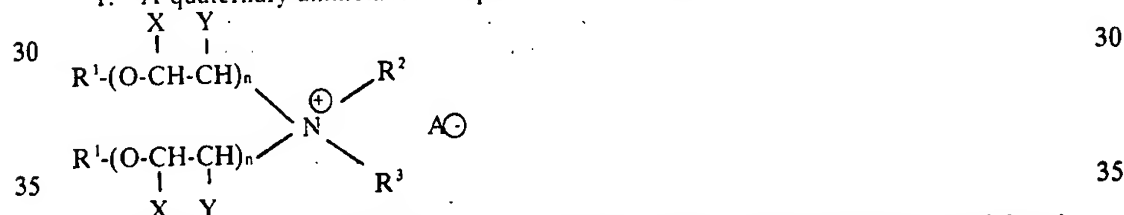
0.2 % of di(pentadecaoxyethyloleyl)-dimethyl-ammonium chloride

25 28 % of ethyl alcohol 25

ad 100 % of fluorinated hydrocarbons as propellant gas.

WHAT WE CLAIM IS:

1. A quaternary ammonium compound of the formula



in which each R^1 is an alkyl or alkenyl group having from 8 to 24 carbon atoms, a cyclohexyl group or an aryl group which may be substituted by one or more alkyl groups, each X and Y is a hydrogen atom or a methyl group with the proviso that X and Y cannot both be methyl groups in the same alkyleneoxy group, each n is an integer from 1 to 20, each of R^2 and R^3 is an alkyl group having from 1 to 4 carbon atoms or a benzyl group, and AC^- is a methylsulfate, ethylsulfate, methylphosphate, chloride or bromide ion.

2. A compound as claimed in claim 1, in which X and Y are both hydrogen atoms.

3. A compound as claimed in claim 1 or claim 2, in which R^2 and R^3 is a methyl or ethyl group.

4. A process for the preparation of a quaternary ammonium compound as claimed in claim 1, which comprises reacting one mole of a secondary etheramine of the formula



in which R^1 , X, Y and n have the meanings specified in claim 1, with one mole each of compounds of the formula R^2A and R^3A in which R^2 , R^3 and A have the meanings specified in claim 1, in the presence of an alkali metal base.

5. A process as claimed in claim 4, wherein the reaction is carried out in a solvent.

60 6. A process as claimed in claim 4 carried out substantially as described in any one of 60 Examples 1 to 7 herein.

7. A quaternary ammonium compound as claimed in claim 1 whenever prepared by a process as claimed in any one of claims 4 to 6.

8. A hair care or fabric softening composition comprising an aqueous and/or alcoholic

solution or dispersion of one or more quaternary ammonium compounds as claimed in claim 1.

9. A hair care composition substantially as described in any one of Examples 8 to 16 herein.

5 10. A fabric softening composition comprising from 1 to 15 % by weight of one or more compounds as claimed in claim 1 in aqueous solution or dispersion. 5

11. A fabric softening composition comprising from 20 to 35% by weight of one or more compounds as claimed in claim 1 in aqueous solution or dispersion.

10 12. A method for treating the hair, which comprises applying thereto a hair care composition as claimed in claim 8 or claim 9. 10

13. A method for softening a textile fabric, which comprises applying thereto a fabric softening composition as claimed in claim 8 or claim 10.

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